

BLEACHING OF MEDIUM CONSISTENCY PULP WITH OZONE
WITHOUT HIGH SHEAR MIXING

Field of the invention

The invention relates to a method for bleaching medium consistency pulp with an ozone-containing gas. In particular, the invention relates to the proper utilization of the very fast reaction of ozone, by providing efficient but pulp-preserving mixing immediately on introducing a substantial amount of ozone into the pulp.

Background of the invention

A number of methods for the bleaching of pulp with ozone is known in the art. These methods have developed towards carrying out the bleaching stage with medium consistency pulp, i.e. having a consistency of about 7 - 16 per cent.

Generally, ozone bleaching of medium consistency (MC) pulp according to current practice can be described as ozone generation followed by compression before introducing the ozone containing gas into the the MC pulp flow. The gas-liquid-fiber suspension is vigorously treated in one or several high shear mixers before the suspension is lead to a bleach tower. The ozone may be introduced at several points along the pulp stream. Vent gases must be treated because of excess ozone carried over.

The principle described may be a result of the application of oxygen bleaching methods. Oxygen, however, operates at a much slower rate, and the temperatures used are significantly higher than those employed in ozone bleaching.

Typical and frequent problems arise from the difficulty to keep the suspension uniform. Segregation into two-phase flow easily occurs, and the ozonisation rate drops significantly (to 1 or even 0.1 % of its optimum rate) This is a dominant problem, which may be reduced by using a higher quality ozone, resulting in less gas void and consequently less need for vigorous mixing. A typical solution in the present state of the art is the use of more than one mixer. This does not, however, eliminate the problem, and by applying more shear forces to the pulp, the strength properties of the resulting product are severely affected.

A basic problem with such mixers is the short residence time, and if mixing time is increased, undesired backmixing may occur.

After leaving the mixers, the gas-pulp suspension soon segregates into two-phase flow having a relatively small gas-liquid interface per unit volume. The chemical consequences of this are low capacity and a non-uniform bleaching result. Obvious evidence of this phenomenon is the significant ozone surplus often remaining after the bleaching stage, representing both a hazard and an economical loss.

Description of the prior art

A pulp bleaching method comprising introduction of high pressure ozone in a carrier gas into a pulp stream with vigorous mixing and subsequent removal of carrier gas is disclosed in, e.g. EP-A 511 433. The major issue of this document is the removal of gas from the pulp after injection into the mixer; the reaction is said to take place essentially within ten seconds in a vertical reaction vessel situated immediately following the fluidizing mixer. Gas at about 10-13 bar containing about 3-10 % ozone by weight (6.8 vol %) is used. Preferably, the gas-pulp mixture is carried in a horizontal path following the vertical reaction step to effect separation of the large amount of carrier gas involved.

Austrian patent application 2203/92 describes a method wherein medium consistency pulp is treated with an ozone-containing gas comprising more than 120 g O₃ / normal m³ gas (5.6 vol %) whereby the gas is introduced as fine bubbles with a low differential pressure (preferably less than 1 bar). It is considered that using gas with a high ozone content, a sufficient amount of ozone is can be suspended into the gas to achieve the desired bleaching. Further, AT 2203/92 discloses the use of mixers with or without fluidisation effects, and of an ozone reaction stage subsequent to the mixing stage, as well as additional ozone addition stages with degassing stages in between. Characteristically, the highly concentrated ozone is introduced in static mixers at several points, possibly removing the inert carrier gas (normally oxygen) between stages, and the final reaction between ozone and fiber takes place in a bleach reactor, typically of the traditional upflow tower type.

A common feature of several other publications disclosing ozone bleach processes for medium consistency pulp is the use of fluidizing mixers in connection with the injection

of ozone-carrying gas, and the use of subsequent, relatively extended reaction stages and gas separation.

In chemical process terms, MC ozonisation can be described as ozone molecules in a gas phase that must be transported to the vicinity of the fiber and react with the fiber or other substrates. The ozone must diffuse through the gas-liquid interface, through the liquid to the fiber. The applied mixing affects the size and the relative velocity of the gas bubbles, and also the amount of fiber-liquid interface. The rate limiting step completely dominating the interaction of ozone with the fiber material is the transport of ozone through the gas-liquid interface. The gas-liquid transfer rate in a given volume is heavily dependant on the bubble size, i.e. gas-liquid surface area m^2 gas/ m^3 suspension, and on the partial pressure of ozone. Other rate limiting steps, like diffusion in the fiber material itself, are determined by the nature and the consistency of the pulp, which is dominantly affected by the temperature.

Due to its dependency on mass transfer, the reaction rate of ozone is, theoretically and empirically, first order.

Consequently, efficient process solutions must be characterized by that

- the residence time distribution (RTD) must follow a plug-flow pattern (in contrast, backmixing commonly occurs in mixers), which requires special reactor geometry to avoid backmixing e.g appropriate turbine and baffles.
- mean residence time in transfer/mixer/reactor must match transport and reaction times for complete conversion of ozone; consequently reactor diameter, shape and rotation rate of a possible turbine must match flow rate.
- all ozone should be introduced in one step.

The high gas void, i.e. the low concentration of ozone generated by most present ozone generators, limits the possibilities to improve the situation. Reduced gas void in subsequent generations of ozone generators will reduce the need for mixing and reduce energy requirements as well as the size of the equipment. Higher ozone concentrations will also increase the ozonisation rate.

Disclosure of the invention

According to the method of the present invention, high-concentration, high pressure ozone is introduced into the pulp line, whereby conditions approaching plug flow are achieved, a high concentration of ozone is reached with a mass transfer area in the suspension which is sufficient for effective delignification.

According to one aspect of the present invention, the ozone is introduced using effective injection nozzles providing for the efficient dispersion necessary for obtaining a uniform distribution as well as sufficient mass transfer area to overcome the rate-delimiting mass transfer threshold present in methods according to the prior art. Thus, the need for fiber-destroying high shear fluidizing mixers is removed.

According to another aspect of the present invention, a dynamic low to medium intensity mixer is provided in the pulp stream immediately downstream of the ozone injection site. Such a mixer delivers to the pulp stream amounts of energy which are well below fluidization energies, and does not mechanically affect the fiber.

With the aid of recent technology, as disclosed in e.g. Swedish Patent Application 9502339-6, ozone with a concentration of up to 18-20 % by volume may be generated. References to concentrations as high as 300 g O₃/Nm³ have been made in prior art publications (e.g. EP-A-426 652, priority 30.10.1989), but such concentrations have not been technically feasible until recently. Using a high ozone concentration (300 g per m³ and higher) and at high pressure (10 bars and higher) together with proper injection technique, the reaction between ozone and fiber is allowed to take place at such a rate that the subsequent use of an upflow bleach tower is not necessary. The gas pressure is obtained by using precompressed oxygen, optionally mixed with other gases or liquids (e.g. argon) to maintain a suitable conductivity for ozone generation.

Oxygen is the most common carrier gas used for ozone. Highly concentrated ozone is usually considered an explosion hazard. As the ozone generating technology has developed, the accepted limit for stable oxygen-ozone mixtures has been repeatedly pushed upwards, and it appears that no absolute concentration limit for the safe handling of ozone has yet been established. Thus, use of very high ozone concentrations may yet be possible, which further facilitates use of methods according to the present invention. According to the present invention, the concentration of ozone in the gas introduced to

the pulp stream is sufficient for achieving bleaching without any fiber-destroying mechanical impact.

The initial distribution of highly concentrated ozone into the pulp is of importance, for the selectivity, as the carbohydrate component itself may be attacked by ozone if exposed for an extended time. The absence of backmixing, as may occur in high shear mixers, and the presence of plug flow conditions counteract this phenomenon.

Description of preferred embodiments

Figure 1 shows a comparison between the changes in reaction rates against time in a prior art ozone pulp bleaching process using a medium consistency mixer, and a process according to the present invention.

Example 1

Ozone-carrying gas having a pressure of about 15 bar and an ozone concentration 14 % by volume is introduced into a medium consistency pulp line carrying 1000 tons/day via a collar of radially arranged nozzles. Preferably, the nozzles are arranged to direct the gas radially into the pulp flow, essentially in a direction perpendicular to the pulp flow. A number of nozzles sufficient for distributing the gas evenly must be used. On this production scale, 186 nozzles with an inlet diameter of maximum 1 mm may be used. A sufficient mean residence time (10-40 seconds) must be allowed before any other disturbing action to the pulp.

Example 2

A medium intensity (low-shear) mixer is adapted into the pulp stream of the previous example, preferably immediately following the gas injection site. The mixer turbine is preferably a double or multiple screw with blade angles and rotation rate balanced to maintain the plug flow residence time distribution (RTD) and giving good radial mixing efficiency. The center blade has a steeper angle than the outer screw blade. Alternatively, porous metal injector devices for introduction of ozone can be arranged peripherally or on the turbine.

Figure 1 shows a comparison between a system employing a traditional medium consistency mixer with a very high capacity for a short interval dropping rapidly to zero, compared to a system according to the invention with a moderately high capacity kept constant for a long period. The dotted line represents state-of-the-art traditional medium consistency mixer technology. The first, steep section shows the effect of the mixer with high reaction and uniform distribution. The low rate section shows the effect of the corruption of the gas-suspension interface. The reaction takes place with a nonuniform distribution and the pulp is mechanically stressed by high shear mixing.

The solid line represents a system according to the invention. Throughout the process, a moderately fast reaction is taking place in a mildly stressed pulp and with a uniform distribution of ozone.

Table 1 shows a comparison in numbers between a typical conventional MC bleaching system, a state-of-the-art system and a system according to the present invention.

Table 1

		Conventional	Modern	Present invention
Calculus Base	Units			
Pulp production	ton OD/day	1000	1000	1000
Consistency	%	10	10	10
Ozone pressure	bar	9	9	15
Ozone concentration	w%	10	14	20
	vol%	7	10	14 = 270
Ozone charge (3-5)	kg/ton OD pulp	5	5	5
Ozone generator	kg/h	208	208	208
Ozone volume flow	m ³ /s			0,0146
Nozzle diameter	m			0,001
Number of nozzles				186
Process				
Process temperature	°C	40	40	40
Process pressure	bar	7	7	15
Pulp Flow	ton OD pulp /h	42	42	42
Volume Flow	m ³ /h MC pulp	375	375	375
Ozone gas charge	m ³ /h at actual press.	234	165	53
Gas void *	%	38	31	12
Equipment		Ozone compres- sor 1-3 mixers Bleach tower	Ozone com- pressor 1+ mixers Bleach tower	No ozone com- pressor No mixer Small bleach reactor

* Note: Gas void is proportional to process problems